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#### (54) PROCESS FOR CONVERTING A SOLID BIOMASS MATERIAL

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See application file for complete search history.

#### (56) References Cited

#### U.S. PATENT DOCUMENTS

#### FOREIGN PATENT DOCUMENTS

CN 1270984 10/2000 CN 101081801 12/2007 (Continued)

OTHER PUBLICATIONS

Ancilotti, F. et al., "MTBE from Butadiene-Rich C4s", Hydrocarbon Processing, 1987, pp. 50-53.

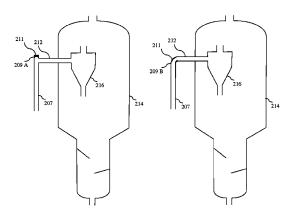
(Continued)

Primary Examiner — Nina Bhat

#### (57) ABSTRACT

A process for converting a solid biomass material is provided. The solid biomass material is contacted with a catalytic cracking catalyst at a temperature of more than 400° C. in a riser reactor to produce one or more cracked products. The riser reactor is an external riser reactor with a curve and/or low velocity zone at its termination and wherein a part of the catalytic cracking catalyst has deposited in the curve and/or low velocity zone.

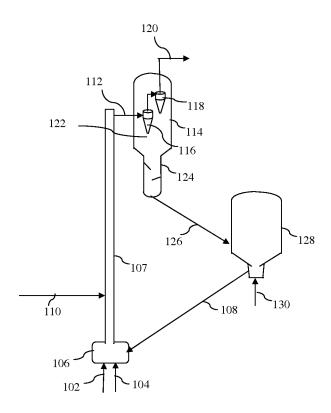
#### 15 Claims, 3 Drawing Sheets

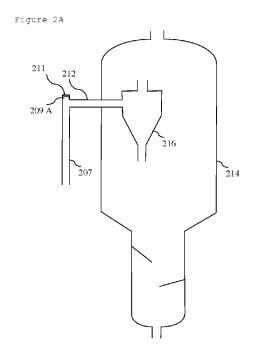


(56) References Cited				WO WO	9718278	5/1997
U.S	S. PATENT	DOCUMENTS		WO	02070630 WO 2005/080531	9/2002 * 9/2005
				WO	2006031011	3/2006
3,639,228 A		Carr et al		WO WO	2006121212	11/2006
4,433,984 A		Gartside et al	96/144	WO	2007090884 2009143017	8/2007 11/2009
4,435,279 A 4,727,214 A		Busch et al. Uytterhoeven et al.		WO	2010002792	1/2010
4,851,109 A		Chen et al.		WO	2010062611	6/2010
4,876,108 A	10/1989	Underwood et al.		WO	2010068255	6/2010
5,580,442 A		Kwon et al.	422/144	WO	2010135734	11/2010
5,622,677 A 6,652,815 B1		Hadjigeorge Sattar			OTHER	PUBLICATIONS
6,971,594 B1		Polifka	722/173			
7,369,294 B2		Gally et al.				Biomass-Derived Osygenates in the Oil
7,531,081 B2		Daniel et al.				(FCC) Reaction Pathways and Role of
7,718,140 B1 8,003,835 B2		Seibert et al. Yanik et al.		-	•	is, 2007, vol. 247, pp. 307-327.
8,013,195 B2		McCall et al.				Derived Feedstock Co-Processing With
8,057,641 B2		Bartek et al.				d-Generation Fuel Production in FCC Environmental, Elsevier, NL, vol. 96,
8,063,258 B2		Bartek et al.			-4, 2010, pp. 476-485.	
8,207,385 B2 8,288,599 B2		O'Connor et al. Yanik et al.				Pyrolysis of Biomass for Biofuels Pro-
8,288,600 B2		Bartek et al.				chnology, Elsevier, NL, vol. 91, No. 1,
8,349,170 B2		Tammera et al	208/113		рр. 25 <b>-</b> 32.	
8,455,705 B2		Cortright et al.				neries-Synergies between Bio and Oil
8,524,960 B2 8,558,043 B2	10/2013	O'Connor et al. Yanik et al.				of Fuels from Biomass", Angewandte 007) vol. 46; pp. 7184-7201.
8,748,680 B2		Hogendoom et al.				ss Pyrolysis in a Circulating Fluid Bed
2008/0022595 A1		Lemaire et al.				Fuels and Chemicals", 2002, Fuel, vol.
2008/0035526 A1 2008/0058572 A1		Hedrick et al. Fernandez et al.			2087-2095.	, , ,
2008/0038372 A1 2008/0134892 A1		Claude				'Influence of Reaction Temperature,
2008/0216655 A1	9/2008	Vimalchand et al.				emoval System on the Production of
2009/0013603 A1		Rolland				Fast Pyrolysis, Using a Fluidized Bed", 5, 2005, pp. 2179-2184.
2009/0026112 A1 2009/0142241 A1		Dierickx et al. Huziwara et al.				atalytic Cracking", Science & Technol-
2009/0253948 A1		McCall et al.			993, p. 391.	and the Checking , serence & reemier
2009/0283445 A1		Tammera et al.				Zeolite Structure Types", 4th Rev. ED,
2010/0076096 A1		Calis et alYanik et al.	518/702		s vol. 17:A1-A6, 1996	
2010/0105970 A1 2010/0163455 A1		Hadjigeorge et al.				atalytic Cracking Handbook: Design,
2010/0222620 A1		O'Connor et al.		223.	ion, and froubleshoot	ing of FCC Facilities", 1995, pp. 219-
2011/0138681 A1		Ramirez Corredores et al	l.		makers P Let al '	"Comparison of Comprehensive Two-
2011/0154720 A1 2011/0224471 A1		Bartek et al. Wormsbecher et al.				graphy and Gas Chromatography-Mass
2011/0251047 A1		Niccum et al.		Spectro	ometry for the Chara	cterization of Complex Hydrocarbon
2012/0022307 A1		Yanik et al.				atography A, vol. 892, 2000, pp. 29-46.
2012/0160741 A1		Gong et al. O'Connor et al.				tic Cracking Technology and Opera-
2012/0198756 A1	0/2012	O Comioi et al.			997, Chapter 4, pp. 11	nsfer Line"; Fluid Catalytic Cracking
FOREIGN PATENT DOCUMENTS				Technology & Operations, 1997, Chapter 8, pp. 223-235.		
						Design and Operation", Fluid Catalytic
	58135	10/2009		Cracki	ng Technology & Ope	rations, 1997 Chapter 3, pp. 101-112.
	324330 31163	9/2010 8/1987				ation", Fluid Catalytic Cracking Tech-
EP 0321305		6/1989		nology 186-19		Chapter 3, pp. 104-120 & Chapter 6, pp.
EP 0649896 10/1994					Biomass Pyrolysis Oil Properties and	
EP 0668342 8/1995					cy Conversion and Management, 2007,	
EP 0699225 B1 2/1999 EP 0994173 9/1999				, pp. 87-92.		
EP 0705321 3/2000					ffice of the People's Republic of China	
EP 1892280 2/2008					nd Office Action, for related case Ref.	
EP 1903019 11/2008 EP 2053114 4/2009					application No. 201280026622.0.	
	07100	10/2009				ffice of the People's Republic of China or related case Ref. TS2627-CN-PCT,
EP 21	EP 2108637 10/2009				e Application No. 201	
	66663	5/1986				ffice of the People's Republic of China
GB 2371807 8/2002 GB 2386607 9/2003		8/2002 9/2003		-		for related case Ref. TS2619-CN-PCT,
GB 2447684 9/2008				e Application No. 201		
WO 92	06848	4/1992				ffice of the People's Republic of China 2nd Office Action, for related case Ref.
	21139	10/1993		~		application No. 201280027542.7.
	126848 100604	11/1994 1/1995			5 _, 5 mmese /1	11
	00604	1/1996		* cited	l by examiner	

<sup>\*</sup> cited by examiner

Figure 1





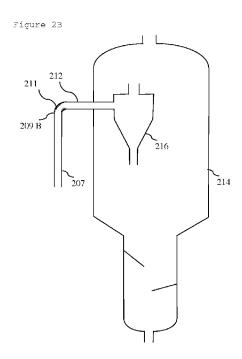
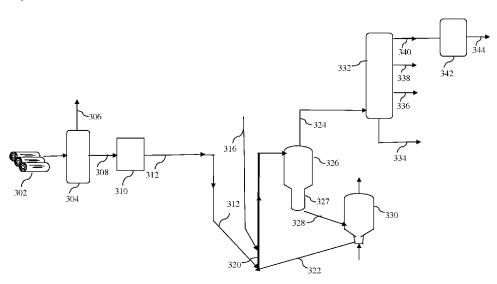


Figure 3



# PROCESS FOR CONVERTING A SOLID BIOMASS MATERIAL

The present application claims the benefit of European Patent Application No. 11163425.9, filed Apr. 21, 2011 the ontire disclosure of which is hereby incorporated by reference.

#### FIELD OF THE INVENTION

The invention relates to a process for converting a solid biomass material and a process for producing a biofuel and/or biochemical.

#### BACKGROUND TO THE INVENTION

With the diminishing supply of crude mineral oil, use of renewable energy sources is becoming increasingly important for the production of liquid fuels. These fuels from renewable energy sources are often referred to as biofuels.

Biofuels derived from non-edible renewable energy sources, such as cellulosic materials, are preferred as these do not compete with food production. These biofuels are also referred to as second generation, renewable or advanced, biofuels. Most of these non-edible renewable energy sources, 25 however, are solid materials that are cumbersome to convert into liquid fuels.

For example, the process described in WO 2010/062611 for converting solid biomass to hydrocarbons requires three catalytic conversion steps. First the solid biomass is contacted 30 with a catalyst in a first riser operated at a temperature in the range of from about 50 to about 200° C. to produce a first biomass-catalyst mixture and a first product comprising hydrocarbons (referred to as pretreatment). Hereafter the first biomass-catalyst mixture is charged to a second riser oper- 35 ated at a temperature in the range of from about 200° to about 400° C. to thereby produce a second biomass-catalyst mixture and a second product comprising hydrocarbons (referred to as deoxygenating and cracking); and finally the second biomass-catalyst mixture is charged to a third riser operated at 40 a temperature greater than about 450° C. to thereby produce a spent catalyst and a third product comprising hydrocarbons. The last step is referred to as conversion to produce the fuel or specialty chemical product. WO 2010/062611 mentions the possibility of preparing the biomass for co-processing in con- 45 ventional petroleum refinery units. The process of WO 2010/ 062611, however, is cumbersome in that three steps are needed, each step requiring its own specific catalyst.

WO2010/135734 describes a method for co-processing a biomass feedstock and a refinery feedstock in a refinery unit comprising catalytically cracking the biomass feedstock and the refinery feedstock in a refinery unit comprising a fluidized reactor, wherein hydrogen is transferred from the refinery feedstock to carbon and oxygen of the biomass feedstock. In one of the embodiments WO2010/135734 the biomass feedstock comprises a plurality of solid biomass particles having an average size between 50 and 1000 microns. In passing, it is further mentioned that solid biomass particles can be preprocessed to increase brittleness, susceptibility to catalytic conversion (e.g. by roasting, toasting, and/or torrefication) 60 and/or susceptibility to mixing with a petrochemical feedstock.

In the article titled "Biomass pyrolysis in a circulating fluid bed reactor for production of fuels and chemicals" by A. A. Lappas et al, published in Fuel, vol. 81 (2002), pages 2087-65 2095, an approach for biomass flash pyrolysis in a circulating fluid bed (CFB) reactor is described. The CFB reactor com2

prised a vertical riser type reactor (7.08 mm ID). The riser height was 165 cm. From FIG. 1, the riser reactor appears to be an essentially vertical external riser reactor connected via an essentially horizontal cross-over pipe with a stripper vessel. The vertical external riser reactor and horizontal crossover pipe appear connected via a 90 degree junction. In all experiments lignocell HBS 150-500 supplied by Rettenmaier GmbH (particle size 200-400 micrometer) was used as biomass feedstock. In the conventional biomass pyrolysis tests silica sand was used as a heat carrier. Catalytic biomass pyrolysis was performed using a commercial equilibrium FCC catalyst supplied by a Greek refinery. The Biomass pyrolysis experiments were performed at riser temperatures in the range of 400-500° C. Each biomass pyrolysis run 15 required 2 hour for the line out and the heating up of the unit and 3 hours of a steady state operation. Such operation times are considered to be too short to create any substantial deposition of catalyst.

It would be an advancement in the art to improve the above processes further. For example, in order to scale up the catalytic cracking of the solid biomass feedstock to a commercial scale, the process may require improvements to meet nowadays conversion, robustness maintenance and/or safety requirements.

#### SUMMARY OF THE INVENTION

Such an improvement has been achieved with the process according to the invention. It has been advantageously found that when using an external riser reactor with a curve and/or low velocity zone at its upper end, wherein a part of the catalytic cracking catalyst has deposited in the curve and/or low velocity zone a safer process that may be operated for a longer period can be obtained.

Accordingly in an embodiment provides a process for converting a solid biomass material, comprising contacting the solid biomass material with a catalytic cracking catalyst at a temperature of more than 400° C. in a riser reactor to produce one or more cracked products, wherein the riser reactor is an external riser reactor with a curve and/or low velocity zone at its termination and wherein a part of the catalytic cracking catalyst has deposited in the curve and/or low velocity zone.

Without wishing to be bound by any kind of theory, it is believed that when connecting an upstream external riser reactor with a downstream cross-over pipe in a 90 degrees junction (as described by Lappas et al.) turbulence will be created in the junction.

It has now for the first time been recognized that such turbulence may cause a problem when a solid biomass material is converted.

In the process according to the invention the solid biomass material may be converted into an intermediate oil product (herein also referred to as pyrolysis oil) which intermediate oil product in turn can be cracked into one or more cracked products. Any unconverted solid biomass material particles, however, may cause erosion of the hardware due to the above described turbulence.

The process according to the invention, using an external riser reactor with a curve and/or low velocity zone wherein a part of the catalytic cracking catalyst has deposited in the curve and/or low velocity zone allows one to reduce the risk of erosion, thereby increasing safety and hardware integrity.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a schematic diagram of an embodiment for converting a solid biomass material.

FIG. 2A shows a schematic diagram of specific embodiment A for the process of FIG. 1.

FIG. 2B shows a schematic diagram of specific embodiment B for the process of FIG. 1.

FIG. 3 shows a schematic diagram of another embodiment 5 for converting a solid biomass material.

#### DETAILED DESCRIPTION OF THE INVENTION

Without wishing to be bound to any kind of theory it is 10 believed that the curve and/or low velocity zone reduces the impact by residual solid biomass material particles and the deposited catalytic cracking catalyst forms a protective layer against erosion by unconverted solid biomass material particles.

In addition, the curve and/or low velocity zone, with deposited catalytic cracking catalyst may assist in reducing corrosion due to oxygen-containing compounds in the intermediate oil product or in the one or more cracked products.

The process according to the invention is simple and may 20 require a minimum of processing steps to convert a solid biomass material to a biofuel component and/or biochemical component. Such biofuel component may be fully fungible.

Furthermore the process according to the invention may be easily implemented in existing refineries.

In addition, the process according to the invention does not need any complicated actions, for example it does not need a pre-mixed composition of the solid biomass material and the catalyst.

The one or more cracked products produced by the process 30 according to the invention may be used as an intermediate to prepare a biofuel and/or biochemical component.

The biofuel and/or biochemical component(s) may advantageously be further converted to and/or blended with one or more further components into novel biofuels and/or bio- 35 chemicals.

The process according to the invention therefore also provides a more direct route via catalytic cracking of solid biomass material to second generation, renewable or advanced, biofuels and/or biochemicals.

By a solid biomass material is herein understood a solid material obtained from a renewable source. By a renewable source is herein understood a composition of matter of biological origin. Preferably the renewable source is a composition of matter of cellulosic or lignocellulosic origin as 45 opposed to a composition of matter obtained or derived from petroleum, natural gas or coal.

Preferably the renewable source is a composition of matter of cellulosic or lignocellulosic origin. Any solid biomass material may be used in the process of the invention. In a 50 preferred embodiment the solid biomass material is not a material used for food production. Examples of preferred solid biomass materials include aquatic plants and algae, agricultural waste and/or forestry waste and/or paper waste and/or plant material obtained from domestic waste.

Preferably the solid biomass material contains cellulose and/or lignocellulose. Examples of suitable cellulose-and/or lignocellulose-containing materials include agricultural wastes such as corn stover, soybean stover, corn cobs, rice straw, rice hulls, oat hulls, corn fibre, cereal straws such as 60 wheat, barley, rye and oat straw; grasses; forestry products and/or forestry residues such as wood and wood-related materials such as sawdust; waste paper; sugar processing residues such as bagasse and beet pulp; or mixtures thereof. More preferably the solid biomass material is selected from the 65 group consisting of wood, sawdust, straw, grass, bagasse, corn stover and/or mixtures thereof.

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The solid biomass material may have undergone drying, torrefaction, steam explosion, particle size reduction, densification and/or pelletization before being contacted with the catalyst, to allow for improved process operability and economics.

Preferably the solid biomass material is a torrefied solid biomass material. In a preferred embodiment the process according to the invention comprises a step of torrefying the solid biomass material at a temperature of more than  $200^{\circ}$  C. to produce a torrefied solid biomass material that is contacted with the catalytic cracking catalyst. The words torrefying and torrefaction are used interchangeable herein.

By torrefying or torrefaction is herein understood the treatment of the solid biomass material at a temperature in the range from equal to or more than 200° C. to equal to or less than 350° C. in the essential absence of a catalyst and in an oxygen-poor, preferably an oxygen-free, atmosphere. By an oxygen-poor atmosphere is understood an atmosphere containing equal to or less than 15 vol. % oxygen, preferably equal to or less than 10 vol. % oxygen and more preferably equal to or less than 5 vol. % oxygen. By an oxygen-free atmosphere is understood that the torrefaction is carried out in the essential absence of oxygen.

Torrefying of the solid biomass material is preferably carried out at a temperature of more than 200° C., more preferably at a temperature equal to or more than 210° C., still more preferably at a temperature equal to or more than 220° C., yet more preferably at a temperature equal to or more than 230° C. In addition torrefying of the solid biomass material is preferably carried out at a temperature less than 350° C., more preferably at a temperature equal to or less than 330° C., still more preferably at a temperature equal to or less than 310° C., yet more preferably at a temperature equal to or less than 300° C.

Torrefaction of the solid biomass material is preferably carried out in the essential absence of oxygen. More preferably the torrefaction is carried under an inert atmosphere, containing for example inert gases such as nitrogen, carbon dioxide and/or steam; and/or under a reducing atmosphere in the presence of a reducing gas such as hydrogen, gaseous hydrocarbons such as methane and ethane or carbon monoxide.

The torrefying step may be carried out at a wide range of pressures. Preferably, however, the torrefying step is carried out at atmospheric pressure (about 1 bar, corresponding to about 0.1 MegaPascal).

The torrefying step may be carried out batchwise or continuously.

The torrefied solid biomass material has a higher energy density, a higher mass density and greater flowability, making it easier to transport, pelletize and/or store. Being more brittle, it can be easier reduced into smaller particles.

Preferably the torrefied solid biomass material has an oxygen content in the range from equal to or more than 10 wt %, more preferably equal to or more than 20 wt % and most preferably equal to or more than 30 wt % oxygen, to equal to or less than 60 wt %, more preferably equal to or less than 50 wt %, based on total weight of dry matter (i.e. essentially water-free matter).

In a further preferred embodiment, any torrefying or torrefaction step further comprises drying the solid biomass material before such solid biomass material is torrefied. In such a drying step, the solid biomass material is preferably dried until the solid biomass material has a moisture content in the range of equal to or more than 0.1 wt % to equal to or less than 25 wt %, more preferably in the range of equal to or more than 5 wt % to equal to or less than 20 wt %, and most preferably

in the range of equal to or more than 5 wt % to equal to or less than 15 wt %. For practical purposes moisture content can be determined via ASTM E1756-01 Standard Test method for Determination of Total solids in Biomass. In this method the loss of weight during drying is a measure for the original 5 moisture content.

Preferably the solid biomass material is a micronized solid biomass material. By a micronized solid biomass material is herein understood a solid biomass material that has a particle size distribution with a mean particle size in the range from equal to or more than 5 micrometer to equal to or less than 5000 micrometer, as measured with a laser scattering particle size distribution analyzer. In a preferred embodiment the process according to the invention comprises a step of reducing the particle size of the solid biomass material, optionally 15 before or after such solid biomass material is torrefied. Such a particle size reduction step may for example be especially advantageous when the solid biomass material comprises wood or torrefied wood. The particle size of the, optionally torrefied, solid biomass material can be reduced in any man- 20 and/or optionally torrefied, solid biomass material can be ner known to the skilled person to be suitable for this purpose. Suitable methods for particle size reduction include crushing, grinding and/or milling. The particle size reduction may preferably be achieved by means of a ball mill, hammer mill, (knife) shredder, chipper, knife grid, or cutter.

Preferably the solid biomass material has a particle size distribution where the mean particle size lies in the range from equal to or more than 5 micrometer (micron), more preferably equal to or more than 10 micrometer, even more preferably equal to or more than 20 micrometer, and most 30 preferably equal to or more than 100 micrometer to equal to or less than 5000 micrometer, more preferably equal to or less than 1000 micrometer and most preferably equal to or less than 500 micrometer.

Most preferably the solid biomass material has a particle 35 size distribution where the mean particle size is equal to or more than 100 micrometer to avoid blocking of pipelines and/or nozzles. Most preferably the solid biomass material has a particle size distribution where the mean particle size is equal to or less than 3000 micrometer to allow easy injection 40 into the riser reactor.

For practical purposes the particle size distribution and mean particle size of the solid biomass material can be determined with a Laser Scattering Particle Size Distribution Analyzer, preferably a Horiba LA950, according to the ISO 45 13320 method titled "Particle size analysis-Laser diffraction methods".

Hence, preferably the process of the invention comprises a step of reducing the particle size of the solid biomass material, optionally before and/or after torrefaction, to generate a 50 particle size distribution having a mean particle size in the range from equal to or more than 5, more preferably equal to or more than 10 micron, and most preferably equal to or more than 20 micron, to equal to or less than 5000 micron, more preferably equal to or less than 1000 micrometer and most 55 preferably equal to or less than 500 micrometer to produce a micronized, optionally torrefied, solid biomass material.

In another embodiment the particle size reduction of the, optionally torrefied, solid biomass material is carried out in the presence of a liquid hydrocarbon and/or water, to improve 60 processibility and/or avoid dusting. Most preferably such a liquid hydrocarbon is the same as the fluid hydrocarbon envisaged for the fluid hydrocarbon feed in process of the invention. Examples of such a liquid hydrocarbon include mineral oil fractions such as long and short residue.

In a preferred embodiment the, optionally micronized and optionally torrefied, solid biomass material is dried before 6

being supplied to the riser reactor. Hence, if the solid biomass material is torrefied, it may be dried before and/or after torrefaction. If dried before use as a feed, the solid biomass material is preferably dried at a temperature in the range from equal to or more than 50° C. to equal to or less than 200° C., more preferably in the range from equal to or more than 80° C. to equal to or less than 150° C. The, optionally micronized and/or torrefied, solid biomass material is preferably dried for a period in the range from equal to or more than 30 minutes to equal to or less than 2 days, more preferably for a period in the range from equal to or more than 2 hours to equal to or less than 24 hours.

In addition to the, optionally micronized and/or optionally torrefied, solid biomass material preferably also a fluid hydrocarbon feed is contacted with the catalytic cracking catalyst in the riser reactor. This fluid hydrocarbon feed can be co-feeded to the external riser reactor and may hereafter also be referred to as fluid hydrocarbon co-feed.

The fluid hydrocarbon feed and the, optionally micronized mixed prior to entry into the riser reactor or they can be added separately, at the same location or different locations to the riser reactor.

In one embodiment the fluid hydrocarbon feed and the, 25 optionally micronized and/or optionally torrefied, solid biomass material are not mixed together prior to entry into the riser reactor. In this embodiment the fluid hydrocarbon feed and the solid biomass material may be fed simultaneously (that is at one location) to the riser reactor, and optionally mixed upon entry of the riser reactor; or, alternatively, the fluid hydrocarbon feed and the solid biomass material may be added separately (at different locations) to the riser reactor. Riser reactors can have multiple feed inlet nozzles. The solid biomass material and the fluid hydrocarbon feed can therefore be processed in the riser reactor even if both components are not miscible by feeding each component through a separate feed inlet nozzle.

In one embodiment the solid biomass material is introduced to the riser reactor at a location downstream of a location where a fluid hydrocarbon feed is introduced to the riser reactor. Without wishing to be bound by any kind of theory it is believed that by allowing the fluid hydrocarbon feed to contact the catalytic cracking catalyst first, hydrogen may be generated. The availability of this hydrogen may assist in the reduction of coke formation when the solid biomass material is contacted with the catalytic cracking catalyst more downstream in the riser reactor.

In another embodiment the solid biomass material is introduced into the riser reactor at a location upstream of the location where the fluid hydrocarbon feed is introduced. This advantageously allows for a longer residence time for the solid biomass material. In addition the solid biomass material can take advantage of the higher temperature and higher catalyst to feed weight ratio at that location. The supply of a solid biomass material into the riser reactor at a location upstream of a location where a fluid hydrocarbon feed is introduced may advantageously increase the conversion of the solid biomass material.

In another embodiment a fluid hydrocarbon feed and the solid biomass material are mixed together prior to entry into the riser reactor to provide a slurry feed comprising the fluid hydrocarbon feed and the solid biomass material. This advantageously allows for easier feeding of the solid biomass material to the riser reactor.

By a hydrocarbon feed is herein understood a feed that contains one or more hydrocarbon compounds. By hydrocarbon compounds are herein understood compounds that con-

tain both hydrogen and carbon and preferably consist of hydrogen and carbon. By a fluid hydrocarbon feed is herein understood a hydrocarbon feed that is not in a solid state. The fluid hydrocarbon co-feed is preferably a liquid hydrocarbon co-feed, a gaseous hydrocarbon co-feed, or a mixture thereof.

The fluid hydrocarbon co-feed can be fed to a catalytic cracking reactor (the riser reactor) in an essentially liquid state, in an essentially gaseous state or in a partially liquid-partially gaseous state. When entering the riser reactor in an essentially or partially liquid state, the fluid hydrocarbon co-feed preferably vaporizes upon entry and preferably is contacted in the gaseous state with the catalytic cracking catalyst and/or the solid biomass material.

For hydrocarbon co-feeds that are highly viscous, it may be advantageous to preheat such feeds before entering the catalytic cracking reactor. For example, hydrocarbon co-feeds such as a long residue, a vacuum gas oil and/or mixtures thereof may be preheated to a temperature equal to or above 250° C.

The fluid hydrocarbon feed can be any non-solid hydrocarbon feed known to the skilled person to be suitable as a feed for a catalytic cracking reactor. The fluid hydrocarbon feed can for example be obtained from a conventional crude oil (also sometimes referred to as a petroleum oil or mineral oil), an unconventional crude oil (that is, oil produced or extracted using techniques other than the traditional oil well method) or a renewable oil (that is, oil derived from a renewable source, such as pyrolysis oil, vegetable oil and/or a liquefied biomass), a Fisher Tropsch oil (sometimes also referred to as a synthetic oil) and/or a mixture of any of these.

In one embodiment the fluid hydrocarbon feed is derived from a, preferably conventional, crude oil. Examples of conventional crude oils include West Texas Intermediate crude oil, Brent crude oil, Dubai-Oman crude oil, Arabian Light crude oil, Midway Sunset crude oil or Tapis crude oil.

More preferably the fluid hydrocarbon feed comprises a fraction of a, preferably conventional, crude oil or renewable oil. Preferred fluid hydrocarbon feeds include straight run (atmospheric) gas oils, flashed distillate, vacuum gas oils (VGO), coker gas oils, diesel, gasoline, kerosene, naphtha, 40 liquefied petroleum gases, atmospheric residue ("long residue") and vacuum residue ("short residue") and/or mixtures thereof. Most preferably the fluid hydrocarbon feed comprises a long residue and/or a vacuum gas oil.

In one embodiment the fluid hydrocarbon feed preferably 45 has a 5 wt % boiling point at a pressure of 1 bar absolute (corresponding to 0.1 MegaPascal), as measured by means of distillation as based on ASTM D86 titled "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure", respectively as measured by on ASTM 50 D1160 titled "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure", of equal to or more than 100° C., more preferably equal to or more than 150° C. An example of such a fluid hydrocarbon feed is vacuum gas oil.

In a second embodiment the fluid hydrocarbon feed preferably has a 5 wt % boiling point at a pressure of 1 bar absolute (corresponding to 0.1 MegaPascal), as measured by means of distillation based on ASTM D86 titled "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure", respectively as measured by on ASTM 60 D1160 titled "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure", of equal to or more than 200° C., more preferably equal to or more than 220° C., most preferably equal to or more than 240° C. An example of such a fluid hydrocarbon feed is long residue.

In a further preferred embodiment equal to or more than 70 wt %, preferably equal to or more than 80 wt %, more pref-

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erably equal to or more than 90 wt % and still more preferably equal to or more than 95 wt % of the fluid hydrocarbon feed boils in the range from equal to or more than 150° C. to equal to or less than 600° C. at a pressure of 1 bar absolute (corresponding to 0.1 MegaPascal), as measured by means of a distillation by ASTM D86 titled "Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure", respectively as measured by on ASTM D1160 titled "Standard Test Method for Distillation of Petroleum Products at Reduced Pressure".

The composition of the fluid hydrocarbon feed may vary widely. The fluid hydrocarbon feed may for example contain paraffins (including naphthenes), olefins and/or aromatics.

Preferably the fluid hydrocarbon feed comprises in the range from equal to or more than 50 wt %, more preferably from equal to or more than 75 wt %, and most preferably from equal to or more than 90 wt % to equal to or less than 100 wt % of compounds consisting only of carbon and hydrogen, based on the total weight of the fluid hydrocarbon feed.

More preferably the fluid hydrocarbon feed comprises equal to or more than 1 wt % paraffins, more preferably equal to or more than 5 wt % paraffins, and most preferably equal to or more than 10 wt % paraffins, and preferably equal to or less than 100 wt % paraffins, more preferably equal to or less than 90 wt % paraffins, and most preferably equal to or less than 90 wt % paraffins, based on the total fluid hydrocarbon feed. By paraffins both normal-, cyclo- and branched-paraffins are understood.

In another embodiment the fluid hydrocarbon feed comprises or consists of a paraffinic fluid hydrocarbon feed. By a paraffinic fluid hydrocarbon feed is herein understood a fluid hydrocarbon feed comprising in the range from at least 50 wt % of paraffins, preferably at least 70 wt % of paraffins, and most preferably at least 90 wt % paraffins, up to and including 100 wt % paraffins, based on the total weight of the fluid hydrocarbon feed.

For practical purposes the paraffin content of all fluid hydrocarbon feeds having an initial boiling point of at least 260° C. can be measured by means of ASTM method D2007-03 titled "Standard test method for characteristic groups in rubber extender and processing oils and other petroleum-derived oils by clay-gel absorption chromatographic method", wherein the amount of saturates will be representative for the paraffin content. For all other fluid hydrocarbon feeds the paraffin content of the fluid hydrocarbon feed can be measured by means of comprehensive multi-dimensional gas chromatography (GCxGC), as described in P. J. Schoenmakers, J. L. M. M. Oomen, J. Blomberg, W. Genuit, G. van Velzen, J. Chromatogr. A, 892 (2000) p. 29 and further.

Examples of paraffinic fluid hydrocarbon feeds include so-called Fischer-Tropsch derived hydrocarbon streams such as described in WO2007/090884 and herein incorporated by reference, or a hydrogen rich feed like hydrotreater product or hydrowax. By Hydrowax is understood the bottoms fraction of a hydrocracker. Examples of hydrocracking processes which may yield a bottoms fraction that can be used as fluid hydrocarbon feed, are described in EP-A-699225, EP-A-649896, WO-A-97/18278, EP-A-705321, EP-A-994173 and U.S. Pat. No. 4,851,109 and herein incorporated by reference.

By "Fischer-Tropsch derived hydrocarbon stream" is meant that the hydrocarbon stream is a product from a Fischer-Tropsch hydrocarbon synthesis process or derived from such product by a hydroprocessing step, i.e. hydrocracking, hydro-isomerisation and/or hydrogenation.

The Fischer-Tropsch derived hydrocarbon stream may suitably be a so-called syncrude as described in for example GB-A-2386607, GB-A-2371807 or EP-A-0321305. Other

suitable Fischer-Tropsch hydrocarbon streams may be hydrocarbon fractions boiling in the naphtha, kerosene, gas oil, or wax range, as obtained from the Fischer-Tropsch hydrocarbon synthesis process, optionally followed by a hydroprocessing step.

The weight ratio of the solid biomass material to fluid hydrocarbon feed may vary widely. For ease of co-processing the weight ratio of fluid hydrocarbon feed to solid biomass material is preferably equal to or more than 50 to 50 (5:5), more preferably equal to or more than 70 to 30 (7:3), still 10 more preferably equal to or more than 80 to 20 (8:2), even still more preferably equal to or more than 90 to 10 (9:1). For practical purposes the weight ratio of fluid hydrocarbon feed to solid biomass material is preferably equal to or less than 99.9 to 0.1 (99.9:0.1), more preferably equal to or less than 95 15 to 5 (95:5). The fluid hydrocarbon feed and the solid biomass material are preferably being fed to the riser reactor in a weight ratio within the above ranges.

The amount of solid biomass material, based on the total supplied to the riser reactor, is preferably equal to or less than 30 wt %, more preferably equal to or less than 20 wt %, most preferably equal to or less than 10 wt % and even more preferably equal to or less than 5 wt %. For practical purposes the amount of solid biomass material present, based on the 25 total weight of solid biomass material and fluid hydrocarbon feed supplied to the riser reactor, is preferably equal to or more than 0.1 wt %, more preferably equal to or more than 1 wt %.

In a preferred embodiment the fluid hydrocarbon feed 30 comprises equal to or more than 8 wt % elemental hydrogen (i.e. hydrogen atoms), more preferably more than 12 wt % elemental hydrogen, based on the total fluid hydrocarbon feed on a dry basis (i.e. water-free basis). A high content of elemental hydrogen, such as a content of equal to or more than 35 8 wt %, allows the hydrocarbon feed to act as a hydrogen donor in the catalytic cracking process. A particularly preferred fluid hydrocarbon feed having an elemental hydrogen content of equal to or more than 8 wt % is Fischer-Tropsch derived waxy raffinate. Such Fischer-Tropsch derived waxy 40 raffinate may for example comprise about 85 wt % of elemental carbon and 15 wt % of elemental hydrogen.

Without wishing to be bound by any kind of theory it is further believed that a higher weight ratio of fluid hydrocarbon feed to solid biomass material enables more upgrading of 45 the solid biomass material by hydrogen transfer reactions.

The solid biomass material is contacted with the catalytic cracking catalyst in an external riser reactor.

By a riser reactor is herein understood an elongated, preferably essentially tube-shaped, reactor suitable for carrying 50 out, preferably fluidized, catalytic cracking reactions. Suitably a fluidized catalytic cracking catalyst flows in the riser reactor from the upstream end to the downstream end of the reactor. The elongated, preferably tube-shaped, reactor is preferably oriented in an essentially vertical manner. Prefer- 55 ably a fluidized catalytic cracking catalyst flows from the bottom of the riser reactor upwards to the top of the riser reactor.

Preferably the riser reactor is part of a catalytic cracking unit (i.e. as a catalytic cracking reactor), more preferably a 60 fluidized catalytic cracking (FCC) unit.

By an external riser reactor is herein understood a riser reactor that is mainly, preferably wholly, located outside a reactor vessel. The external riser reactor can suitably be connected via a so-called crossover to a vessel.

Preferably the external riser reactor comprises a, preferably essentially vertical, riser reactor pipe. Such a riser reac10

tor pipe is located outside a vessel. The riser reactor pipe may suitably be connected via a, preferably essentially horizontal, downstream crossover pipe to a vessel. The downstream crossover pipe preferably has a direction essentially transverse to the direction of the riser reactor pipe. The vessel may suitably be a reaction vessel suitable for catalytic cracking reactions and/or a vessel that comprises one or more cyclone separators and/or swirl separators. Suitably the crossover pipe may also connect directly to a cyclone and/or swirl separator.

It is also possible for the external riser reactor to be part of a so-called U-bend. In such a case one leg of the U-bend may be used as standpipe and the other leg of the U-bend may be used as riser reactor. For example, regenerated catalyst may flow from a catalyst regenerator into an inlet at the upstream top of the U-bend downwardly through the bend and subsequently upwardly to the outlet at the downstream top of the U-bend.

The external riser reactor in the process according to the weight of solid biomass material and fluid hydrocarbon feed 20 invention has a curve and/or low velocity zone at its termination. More suitably, the external riser reactor comprises a riser reactor pipe, which riser reactor pipe is curved at the end or has a low velocity zone at its upper end. The curve and/or low velocity zone may for example connect the riser reactor pipe and the so-called crossover pipe.

> Preferably the external riser reactor is a riser reactor where a fluidized catalytic cracking catalyst flows from the bottom of the riser reactor upwards to the top of the riser reactor. Preferably the external riser reactor therefore has a curve or a low velocity zone located at the upper end of a vertical part of the external riser reactor. Hence, preferably in the external riser reactor a, preferably vertical, riser reactor pipe is used that is curved at the end or that has a low velocity zone at its upper end.

> By a low velocity zone is herein preferably understood a zone or an area within the external riser reactor where the velocity of the, preferably fluidized, catalytic cracking catalyst shows a minimum. The low velocity zone may for example comprise an accumulation space located at the most downstream end of the upstream riser reactor pipe as described above, extending such riser reactor pipe beyond the connection with the crossover pipe. An example of a low velocity zone is the so-called "Blind Tee". In such a low velocity zone the velocity of a fluidized catalytic cracking catalyst is suitably lower than the velocity of such fluidized catalytic cracking catalyst in an external riser reactor pipe situated upstream of the low velocity zone; and suitably also lower than the velocity of such fluidized catalytic cracking catalyst in a crossover pipe situated downstream of the low velocity zone.

> In the curve or low velocity zone, catalytic cracking catalyst may deposit and form a protective layer at the inside wall of the external riser reactor. Without wishing to be bound to any kind of theory it is believed that the curve and/or low velocity zone may reduce the impact by residual solid biomass material particles.

> Further the protective layer of deposited catalytic cracking catalyst may advantageously protect the inside wall of the external riser reactor against erosion and/or abrasion by unconverted solid biomass material. As indicated before, the protective layer may not only protect against erosion and/or abrasion by the catalytic cracking catalyst and any residual solid particles but also may protect against corrosion by any oxygen-containing hydrocarbons.

The external riser reactor may comprise several sections of different diameter. Preferably the external riser reactor comprises a pipe herein also referred to as riser reactor pipe. At the

bottom of the external riser reactor further a bottom section may be present (herein also referred to as "liftpot"), which bottom section preferably has a larger diameter than the riser reactor pipe.

Where applicable, a diameter is herein understood to refer to the inner diameter, as for example the inner (i.e. the internal) diameter of the bottom section or riser reactor pipe. Suitably the inner diameter of the most downstream part of the bottom section is larger than the inner diameter of the most upstream part of the riser reactor pipe. That is, at the connection between the bottom section and the riser reactor pipe, the inner diameter of the bottom section is suitably larger than the inner diameter of the riser reactor pipe. Preferably, the maximum inner diameter of the bottom section is larger than the maximum inner diameter of the riser reactor pipe.

Preferably the riser reactor pipe is fluidly connected to the bottom section. More preferably the riser reactor pipe is fluidly connected at its upstream end to the bottom section. 20 When introducing the solid biomass material at such a bottom section of an external riser reactor, the increased diameter at the bottom advantageously allows one to increase the residence time of the solid biomass material at that part of the external riser reactor. In addition, it allows the solid biomass 25 material to take advantage of the high temperature of the catalytic cracking catalyst and/or high catalyst to feed weight ratio at that location of the external riser reactor.

The introduction of a solid biomass material into a bottom section of the riser reactor, which bottom section may comprise an increased diameter, may advantageously increase the conversion of the solid biomass material. This, in turn, may advantageously lead to less unconverted solid biomass material particles that may cause erosion of the hardware.

In a further preferred embodiment the external riser reactor pipe may have a diameter that increases in a downstream direction to allow for the increasing gas volume generated during the conversion of the solid biomass material. The increase of diameter may be intermittent, resulting in two or more sections of the riser reactor pipe having a fixed diameter, where each preceding section has a smaller diameter than the subsequent section, when going in a downstream direction; the increase of diameter may be gradual, resulting in a gradual increase of the riser reactor pipe diameter in a downstream direction; or the increase in diameter may be a mixture of 45 gradual and intermittent increases.

The length of the external riser reactor may vary widely. For practical purposes the riser reactor preferably has a length in the range from equal to or more than 10 meters, more preferably equal to or more than 15 meters and most preferably equal to or more than 20 meters, to equal to or less than 65 meters, more preferably equal to or less than 55 meters and most preferably equal to or less than 45 meters.

Examples of suitable riser reactors are described in the Handbook titled "Fluid Catalytic Cracking technology and 55 operations", by Joseph W. Wilson, published by PennWell Publishing Company (1997), chapter 3, especially pages 101 to 112, herein incorporated by reference.

In the process according to the invention the solid biomass material is preferably supplied to the external riser reactor at 60 a location upstream of the location where any fluid hydrocarbon feed (if present) is supplied.

Without wishing to be bound by any kind of theory it is believed that this allows the solid biomass material to be contacted with the catalytic cracking catalyst first; allowing 65 the solid biomass material to be converted into an intermediate oil product and allowing this intermediate oil product to be 12

at least partly and preferably wholly vaporized before the catalytic cracking catalyst is quenched by addition of a fluid hydrocarbon feed.

In a preferred embodiment the solid biomass material is supplied to the external riser reactor in the most upstream half, more preferably in the most upstream quarter, and even more preferably at the most upstream tenth of the riser reactor. Most preferably solid biomass material is supplied to the external riser reactor at the bottom of this reactor. Addition of the solid biomass material in the upstream part, preferably the bottom, of the reactor may advantageously result in in-situ water formation at the upstream part, preferably the bottom, of the reactor. The in-situ water formation may lower the hydrocarbon partial pressure and reduce second order hydrogen transfer reactions, thereby resulting in higher olefin yields. Preferably the hydrocarbon partial pressure is lowered to a pressure in the range from 0.3 to 3.3 bar absolute (0.03 to 0.33 MegaPascal); more preferably to a pressure in the range from 0.5 to 2.8 bar absolute (0.05 to 0.28 MegaPascal); still more preferably to a pressure in the range from 0.7 to 2.8 bar absolute (0.07 to 0.28 MegaPascal); and most preferably to a pressure in the range from 1.2 to 2.8 bar absolute (0.12 to 0.28 MegaPascal).

It may be advantageous to also add a lift gas at the bottom of the external riser reactor. Examples of such a liftgas include steam, vaporized oil and/or oil fractions, and mixtures thereof. Steam is most preferred as a lift gas from a practical perspective. However, the use of a vaporized oil and/or oil fraction (preferably vaporized liquefied petroleum gas, gasoline, diesel, kerosene or naphtha) as a liftgas may have the advantage that the liftgas can simultaneously act as a hydrogen donor and may prevent or reduce coke formation. In an especially preferred embodiment both steam as well as vaporized oil and/or a vaporized oil fraction (preferably liquefied petroleum gas, vaporized gasoline, diesel, kerosene or naphtha) are used as a liftgas. In a most preferred embodiment the liftgas consists of steam.

If the solid biomass material is supplied at the bottom of the external riser reactor, is may optionally be mixed with such a lift gas before entry in the riser reactor. If the solid biomass material is not mixed with the liftgas prior to entry into the external riser reactor it may be fed simultaneously with the liftgas (at one and the same location) to the external riser reactor, and optionally mixed upon entry of the external riser reactor; or it may be fed separately from any liftgas (at different locations) to the external riser reactor.

When both solid biomass material and steam are introduced into the bottom of the external riser reactor, the steam-to-solid biomass material weight ratio is preferably in the range from equal to or more than 0.01:1, more preferably equal to or more than 0.05:1 to equal to or less than 5:1, more preferably equal to or less than 1.5:1.

Preferably the temperature in the external riser reactor ranges from equal to or more than 450° C., more preferably from equal to or more than 480° C., to equal to or less than 800° C., more preferably equal to or less than 750° C.

More preferably the temperature at the location where the solid biomass material is supplied to the external riser reactor lies in the range from equal to or more than 500° C., more preferably equal to or more than 550° C., and most preferably equal to or more than 600° C., to equal to or less than 800° C., more preferably equal to or less than 750° C.

Preferably the pressure in the external riser reactor ranges from equal to or more than 0.5 bar absolute to equal to or less than 10 bar absolute (0.05 MegaPascal-1.0 MegaPascal),

more preferably from equal to or more than 1.0 bar absolute to equal to or less than 6 bar absolute (0.1 MegaPascal to 0.6 MegaPascal)

Residence time as referred to in this patent application is based on the vapour residence at outlet conditions, that is, 5 residence time includes not only the residence time of a specified feed (such as the solid biomass material) but also the residence time of its conversion products.

When the solid biomass material has a mean particle size in the range from 100 micrometer to 1000 micron, the total 10 average residence time of the solid biomass material most preferably lies in the range from equal to or more than 1 to equal to or less than 2.5 seconds.

When the solid biomass material has a mean particle size in the range from 30 micrometer to 100 micrometer the total 15 average residence time of the solid biomass material most preferably lies in the range from equal to or more than 0.1 to equal to or less than 1 seconds.

The weight ratio of catalyst to feed (that is the total feed of solid biomass material and, if present, any fluid hydrocarbon 20 feed)—herein also referred to as catalyst: feed ratio—preferably lies in the range from equal to or more than 1:1, more preferably from equal to or more than 2:1 and most preferably from equal to or more than 3:1 to equal to or less than 150:1, more preferably to equal to or less than 100:1, most preferably to equal to or less than 50:1. Further preferably the weight ratio of catalyst to solid biomass material (catalyst: solid biomass material is supplied to the external riser reactor preferably lies in the range from equal to or more than 1:1, more preferably equal to or more than 2:1 to equal to or less than 100:1, more preferably equal to or less than 50:1.

In a preferred embodiment any fluid hydrocarbon feed may be introduced to the catalytic cracking reactor at a location where the solid biomass material already had a residence time 35 in the range from equal to or more than 0.01 seconds, more preferably from equal to or more than 0.05 seconds, and most preferably from equal to or more than 0.1 seconds to equal to or less than 2 seconds, more preferably to equal to or less than 1 seconds, and most preferably to equal to or less than 0.5 40 seconds.

In another preferred embodiment the solid biomass material is introduced to the riser reactor at a location with temperature T1 and any fluid hydrocarbon feed is introduced to the riser reactor at a location with temperature T2 and temperature T1 is higher than temperature T2. Preferably both T1 and T2 are equal to or more than 400° C., more preferably equal to or more than 450° C.

The solid biomass material and, if present, the fluid hydrocarbon feed can be supplied to the riser reactor in any manner 50 known to the person skilled in the art. Preferably, however the solid biomass material is supplied to the riser reactor with the help of a screw feeder.

The catalytic cracking catalyst can be any catalyst known to the skilled person to be suitable for use in a cracking 55 process. Preferably, the catalytic cracking catalyst comprises a zeolitic component. In addition, the catalytic cracking catalyst can contain an amorphous binder compound and/or a filler. Examples of the amorphous binder component include silica, alumina, titania, zirconia and magnesium oxide, or 60 combinations of two or more of them. Examples of fillers include clays (such as kaolin).

The zeolite is preferably a large pore zeolite. The large pore zeolite includes a zeolite comprising a porous, crystalline aluminosilicate structure having a porous internal cell structure on which the major axis of the pores is in the range of 0.62 nanometer to 0.8 nanometer. The axes of zeolites are depicted

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in the 'Atlas of Zeolite Structure Types', of W. M. Meier, D. H. Olson, and Ch. Baerlocher, Fourth Revised Edition 1996, Elsevier, ISBN 0-444-10015-6. Examples of such large pore zeolites include FAU or faujasite, preferably synthetic faujasite, for example, zeolite Y or X, ultra-stable zeolite Y (USY), Rare Earth zeolite Y (=REY) and Rare Earth USY (REUSY). According to the present invention USY is preferably used as the large pore zeolite.

The catalytic cracking catalyst can also comprise a medium pore zeolite. The medium pore zeolite that can be used according to the present invention is a zeolite comprising a porous, crystalline aluminosilicate structure having a porous internal cell structure on which the major axis of the pores is in the range of 0.45 nanometer to 0.62 nanometer. Examples of such medium pore zeolites are of the MFI structural type, for example, ZSM-5; the MTW type, for example, ZSM-12; the TON structural type, for example, theta one; and the FER structural type, for example, ferrierite. According to the present invention, ZSM-5 is preferably used as the medium pore zeolite.

According to another embodiment, a blend of large pore and medium pore zeolites may be used. The ratio of the large pore zeolite to the medium pore size zeolite in the cracking catalyst is preferably in the range of 99:1 to 70:30, more preferably in the range of 98:2 to 85:15.

The total amount of the large pore size zeolite and/or medium pore zeolite that is present in the cracking catalyst is preferably in the range of 5 wt % to 40 wt %, more preferably in the range of 10 wt % to 30 wt %, and even more preferably in the range of 10 wt % to 25 wt % relative to the total mass of the catalytic cracking catalyst.

Preferably, the solid biomass material and any optional fluid hydrocarbon feed are contacted in a cocurrent flow configuration with the catalytic cracking catalyst in the external riser reactor.

In a preferred embodiment the process according to the invention comprises:

- a catalytic cracking step comprising contacting the solid biomass material and optionally the fluid hydrocarbon feed with a catalytic cracking catalyst at a temperature of more than 400° C. in an external riser reactor to produce one or more cracked products and a spent catalytic cracking catalyst; a separation step comprising separating the one or more cracked products from the spent catalytic cracking catalyst;
- a regeneration step comprising regenerating spent catalytic cracking catalyst to produce a regenerated catalytic cracking catalyst, heat and carbon dioxide; and
- a recycle step comprising recycling the regenerated catalytic cracking catalyst to the catalytic cracking step.

The catalytic cracking step is preferably carried out as described herein before. In the external riser reactor the solid biomass material is contacted with the catalytic cracking catalyst.

The separation step is preferably carried out with the help of one or more cyclone separators and/or one or more swirl tubes. Suitable ways of carrying out the separation step are for example described in the Handbook titled "Fluid Catalytic Cracking; Design, Operation, and Troubleshooting of FCC Facilities" by Reza Sadeghbeigi, published by Gulf Publishing Company, Houston Tex. (1995), especially pages 219-223 and the Handbook "Fluid Catalytic Cracking technology and operations", by Joseph W. Wilson, published by PennWell Publishing Company (1997), chapter 3, especially pages 104-120, and chapter 6, especially pages 186 to 194, herein incorporated by reference. The cyclone separators are preferably

operated at a velocity in the range from 18 to 80 meters/second, more preferably at a velocity in the range from 25 to 55 meters/second.

In addition the separation step may further comprise a stripping step. In such a stripping step the spent catalyst may be stripped to recover the products absorbed on the spent catalyst before the regeneration step. These products may be recycled and added to the cracked product stream obtained from the catalytic cracking step.

The regeneration step preferably comprises contacting the spent catalytic cracking catalyst with an oxygen containing gas in a regenerator at a temperature of equal to or more than 550° C. to produce a regenerated catalytic cracking catalyst, heat and carbon dioxide. During the regeneration coke, that can be deposited on the catalyst as a result of the catalytic 15 cracking reaction, is burned off to restore the catalyst activity.

The oxygen containing gas may be any oxygen containing gas known to the skilled person to be suitable for use in a regenerator. For example the oxygen containing gas may be air or oxygen-enriched air. By oxygen enriched air is herein 20 understood air comprising more than 21 vol. % oxygen (O<sub>2</sub>), more preferably air comprising equal to or more than 22 vol. % oxygen, based on the total volume of air.

The heat produced in the exothermic regeneration step is preferably employed to provide energy for the endothermic 25 catalytic cracking step. In addition the heat produced can be used to heat water and/or generate steam. The steam may be used elsewhere in the refinery, for example as a liftgas in the riser reactor.

Preferably the spent catalytic cracking catalyst is regenerated at a temperature in the range from equal to or more than 575° C., more preferably from equal to or more than 600° C., to equal to or less than 950° C., more preferably to equal to or less than 850° C. Preferably the spent catalytic cracking catalyst is regenerated at a pressure in the range from equal to or more than 0.5 bar absolute to equal to or less than 10 bar absolute (0.05 MegaPascal to 1.0 MegaPascal), more preferably from equal to or more than 1.0 bar absolute to equal to or less than 6 bar absolute (0.1 MegaPascal to 0.6 MegaPascal).

The regenerated catalytic cracking catalyst can be recycled 40 to the catalytic cracking step. In a preferred embodiment a side stream of make-up catalyst is added to the recycle stream to make-up for loss of catalyst in the reaction zone and regenerator

In the process according to the invention one or more 45 cracked products are produced. In a preferred embodiment this/these one or more cracked products is/are subsequently fractionated to produce one or more product fractions.

As indicated herein, the one or more cracked products may contain one or more oxygen-containing-hydrocarbons. 50 Examples of such oxygen-containing-hydrocarbons include ethers, esters, ketones, acids and alcohols. In specific the one or more cracked products may contain phenols.

Fractionation may be carried out in any manner known to the skilled person in the art to be suitable for fractionation of 55 products from a catalytic cracking unit. For example the fractionation may be carried out as described in the Handbook titled "Fluid Catalytic Cracking technology and operations", by Joseph W. Wilson, published by PennWell Publishing Company (1997), pages 14 to 18, and chapter 8, 60 especially pages 223 to 235, herein incorporated by reference.

The one or more product fractions may contain one or more oxygen-containing-hydrocarbons. Examples of such oxygen-containing-hydrocarbons include ethers, esters, ketones, 65 acids and alcohols. In specific one or more product fractions may contain phenols and/or substituted phenols.

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In a further embodiment at least one of the one or more product fractions obtained by fractionation are subsequently hydrodeoxygenated to produce a hydrodeoxygenated product fraction. This/these hydrodeoxygenated product fraction(s) may be used as biofuel and/or biochemical component(s).

By hydrodeoxygenation is herein understood reducing the concentration of oxygen-containing hydrocarbons in one or more product fraction(s) containing oxygen-containing hydrocarbons by contacting the one or more product fraction(s) with hydrogen in the presence of a hydrodeoxygenation catalyst. Oxygen-containing hydrocarbons that can be removed include acids, ethers, esters, ketones, aldehydes, alcohols (such as phenols) and other oxygen-containing compounds.

The hydrodeoxygenation preferably comprises contacting of the one or more product fractions with hydrogen in the presence of an hydrodeoxygenation catalyst at a temperature in the range from equal to or more than 200° C., preferably equal to or more than 250° C., to equal to or less than 450° C., preferably equal to or less than 400° C.; at a total pressure in the range of equal to or more than 10 bar absolute (1.0 Mega-Pascal) to equal to or less than 350 bar absolute (35 Mega-Pascal); and at a partial hydrogen pressure in the range of equal to or more than 5 bar absolute (0.5 Mega-Pascal) to equal to or less than 350 bar absolute (35 Mega-Pascal).

The hydrodeoxygenation catalyst can be any type of hydrodeoxygenation catalyst known by the person skilled in the art to be suitable for this purpose.

The hydrodeoxygenation catalyst preferably comprises one or more hydrodeoxygenation metal(s), preferably supported on a catalyst support.

Most preferred are hydrodeoxygenation catalysts comprising Rhodium on alumina(Rh/Al<sub>2</sub>O<sub>3</sub>), Rhodium-Cobalt on alumina (RhCo/Al<sub>2</sub>O<sub>3</sub>), Nickel-Copper on alumina (NiCu/Al<sub>2</sub>O<sub>3</sub>), Nickel-Tungsten on alumina (NiW/Al<sub>2</sub>O<sub>3</sub>), Cobalt-Molybdenum on alumina(CoMo/Al<sub>2</sub>O<sub>3</sub>) or Nickel-Molybdenum on alumina (NiMo/Al<sub>2</sub>O<sub>3</sub>).

If the one or more product fractions also contain one or more sulphur-containing hydrocarbons it may be advantageous to use a sulphided hydrodeoxygenation catalyst. If the hydrodeoxygenation catalyst is sulphided the catalyst may be sulphided in-situ or ex-situ.

In addition to the hydrodeoxygenation, the one or more product fractions may be subjected to hydrodesulphurization, hydrodenitrogenation, hydrocracking and/or hydroisomerization. Such hydrodesulphurization, hydrodenitrogenation, hydrocracking and/or hydroisomerization may be carried out before, after and/or simultaneously with the hydrodeoxygenation.

In a preferred embodiment the one or more hydrodeoxygenated product(s) produced in the hydrodeoxygenation can be blended with one or more other components to produce a biofuel and/or a biochemical. Examples of one or more other components with which the one or more hydrodeoxygenated product(s) may be blended include anti-oxidants, corrosion inhibitors, ashless detergents, dehazers, dyes, lubricity improvers and/or mineral fuel components.

Alternatively the one or more hydrodeoxygenated product(s) can be used in the preparation of a biofuel component and/or a biochemical component. In such a case the biofuel component and/or biochemical component prepared from the one or more hydrodeoxygenated product may be subsequently blended with one or more other components (as listed above) to prepare a biofuel and/or a biochemical.

By a biofuel respectively a biochemical is herein understood a fuel or a chemical that is at least party derived from a renewable energy source.

In FIG. 1 an embodiment according to the invention is illustrated. In FIG. 1, a feed of solid biomass material (102) 5 and a steam feed (104) are both introduced into the bottom section (106) of an external reactor riser (107). The external reactor riser (107) is located outside a vessel and comprises a reactor riser pipe, which riser reactor pipe has a curve or low velocity zone at its upper end (in FIG. 1 a low velocity zone as illustrated in FIG. 2A below is shown). In the bottom section (106) of the external reactor riser (107), the solid biomass material (102) and the steam feed (104) are mixed with hot regenerated catalytic cracking catalyst (108). The mixture of catalytic cracking catalyst (108), solid biomass material 15 (102) and steam feed (104) is forwarded into the external riser reactor (107). After about 0.1 seconds of residence time of the solid biomass material (102) in the external reactor riser (107), a fluid hydrocarbon feed (110) is introduced into the external riser reactor (107). In the external reactor riser (107) 20 the solid biomass material (102) and the additional fluid hydrocarbon feed (110) are catalytically cracked to produce one or more cracked products. The mixture of one or more cracked products, catalytic cracking catalyst, steam, some residual non-cracked solid biomass material, and possibly 25 any non-cracked fluid hydrocarbon feed is forwarded from the top of the external riser reactor (107) via a crossover pipe (112) into a reactor vessel (114), comprising a first cyclone separator (116) and a second cyclone separator (118). Cracked products (120) are retrieved via the top of the second 30 cyclone separator (118) and optionally forwarded to a 35ractionators (not shown). Spent catalytic cracking catalyst (122) is retrieved from the bottom of the cyclone separators (116 and 118) and forwarded to a stripper (124) where further cracked products are stripped off the spent catalytic cracking 35

The spent and stripped catalytic cracking catalyst (126) is forwarded to a regenerator (128), where the spent catalytic cracking catalyst is contacted with air (130) to produce a hot regenerated catalytic cracking catalyst (108) that can be 40 recycled to the bottom (106) of the reactor riser (107).

FIGS. 2A and 2B show schematic diagrams of respectively specific embodiment A and specific embodiment B for the process of FIG. 1, where everything is as in the process as illustrated by FIG. 1, except that for FIG. 2B an external 45 reactor riser is used having a curved upper end.

Hence, FIG. 2A shows an external riser reactor (207), comprising a riser reactor pipe with a so-called "Blind Tee" (209A) at its upper end. The external riser reactor (207) is connected via such "Blind Tee" (209A) with a crossover pipe 50 (212). The crossover pipe (212) connects the external riser reactor (207) to a cyclone (216) located in a vessel (214). In the "Blind Tee" (209A) at the upper end of the reactor riser pipe, a deposit (211) of catalytic cracking catalyst has formed, forming an erosion resistant layer protecting the wall 55 of the external reactor riser (207).

FIG. 2B shows an external riser reactor (207), comprising a riser reactor pipe with a curve (209B) at its upper end. The external riser reactor (207) is connected via such curve (209B) with crossover pipe (212). In the curve (209B) at the 60 upper end of the reactor riser pipe, a deposit (211) of catalytic cracking catalyst has formed, forming an erosion resistant layer protecting the wall of the external reactor riser (207).

In FIG. 3 another embodiment according to the invention is illustrated. In FIG. 3, wood parts (302) are fed into a torrefaction unit (304), wherein the wood is torrefied to produce torrefied wood (308) and gaseous products (306) are obtained

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from the top. The torrefied wood (308) is forwarded to a micronizer (310), wherein the torrefied wood is micronized into micronized torrefied wood (312). The micronized torrefied wood (312) is fed directly into the bottom of an external fluidized catalytic cracking (FCC) riser reactor (320) with a curve or low velocity zone at its termination. In addition, a long residue (316) is fed to the external FCC riser reactor (320) at a position located downstream of the entry of the micronized torrefied wood (312). In the FCC riser reactor (320) the micronized torrefied wood (312) is contacted with new and regenerated catalytic cracking catalyst (322) in the presence of the long residue (316) at a catalytic cracking temperature. A mixture of spent catalytic cracking catalyst and produced cracked products is separated in cyclone separators located in vessel (326). The spent catalytic cracking catalyst (328) is forwarded via stripper section (327) to regenerator (330), where it is regenerated and recycled to the bottom of the FCC riser reactor (320) as part of the regenerated catalytic cracking catalyst (322). The cracked products (324) are forwarded to a fractionator (332). In the fractionator (332) the cracked products (324) are fractionated into several product fractions, such as for example, a first fraction, which may be a gasoline containing fraction (340), a second fraction (338), a third fraction (336) and a fourth fraction (334) as shown in the figure. The number of the fractions and each of the fraction cuts may vary depending on the desired product and market demand. The gasoline containing fraction (340) is forwarded to a hydrodeoxygenation reactor (342) where it is hydrodeoxygenated over a sulphided Nickel-Molybdenum on alumina catalyst to produce a hydrodeoxygenated product (344). The hydrodeoxygenated product can be blended with one or more additives to produce a biofuel suitable for use in automotive engines.

What is claimed is:

- 1. A process for converting a solid biomass material, comprising
  - contacting the solid biomass material with a catalytic cracking catalyst at a temperature of more than 400° C. in a riser reactor to produce one or more cracked products, wherein the riser reactor is an external riser reactor with a curve and/or low velocity zone at its termination and wherein a part of the catalytic cracking catalyst has deposited in the curve and/or low velocity zone.
- 2. The process of claim 1 wherein the solid biomass material is fed to the riser reactor as a mixture of solid biomass material and steam.
- 3. The process of claim 1 wherein the riser reactor comprises a riser reactor pipe having a diameter that increases in a downstream direction.
- **4**. The process of claim **1** wherein a fluid hydrocarbon feed is fed into the riser reactor.
- 5. The process of claim 1 wherein the solid biomass material is supplied at the bottom of the riser reactor.
- **6**. The process of claim **1** wherein the riser reactor comprises a bottom section and a riser reactor pipe and wherein the bottom section has a larger diameter than the riser reactor pipe.
- 7. The process of claim 1 wherein the external riser reactor comprises a riser reactor pipe, which riser reactor pipe is curved at the end or which riser reactor pipe has a low velocity zone at its upper end.
- **8**. The process of claim **7** wherein the riser reactor pipe is connected via the curve or low velocity zone to a downstream crossover pipe.
- **9**. The process of claim **1** wherein the fluid hydrocarbon feed is introduced to the riser reactor at a location where the

solid biomass material already had a residence time in the range from equal to or more than 0.1 seconds to equal to or less than 1 seconds.

- 10. The process of claim 1 wherein the ratio between the residence time for the solid biomass material to the residence 5 time for the fluid hydrocarbon feed (residence solid biomass: residence hydrocarbon ratio) lies in the range from equal to or more than 1.01:1 to equal to or less than 2:1.
- 11. The process of claim 1 wherein the solid biomass material is introduced to the riser reactor at a location with 10 temperature T1 and the fluid hydrocarbon feed is introduced to the riser reactor at a location with temperature T2 and temperature T1 is higher than temperature T2.
- 12. The process of claim 1 wherein the one or more cracked products is/are subsequently fractionated to produce one or 15 more product fractions.
- 13. The process of claim 12 wherein the one or more product fractions obtained by fractionation are subsequently hydrodeoxygenated to obtain one or more hydrodeoxygenated products.
- 14. The process of claim 12 wherein the one or more product fractions are blended with one or more other components to prepare a biofuel and/or a biochemical.
- 15. The process of claim 13 wherein the one or more hydrodeoxygenated product fractions are blended with one or 25 more other components to prepare a biofuel and/or a biochemical.

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